C.I. REACTIVE BLACK 5 DEGRADATION BY ADVANCED ELECTROCHEMICAL OXIDATION PROCESS, AEOP

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ABSTRACT
In the last decades, an increasing number of procedures to remove pollutants from wastewater have been reported. Advanced oxidation processes (AOPs) are one of those technologies used for this purpose, namely, for textile wastewater treatment. AOPs are environmentally friendly methods based on chemical, photochemical or photocatalytical production of hydroxyl radical ($HO^{\bullet}$). This strong oxidant can react with most organic compounds present in wastewater, as dyestuffs. In this paper, an Advanced Electrochemical Oxidation Process (AEOP) is discussed concerning the electrochemical degradation of a vinylsulphone reactive dye, C.I. Reactive Black 5, in the presence of hydrogen peroxide and copper ions. The reaction between H_2O_2 and electrochemically generated Cu^{+} ions leads to the production of hydroxyl radicals, causing dye oxidation and degradation. The efficiency of the process is followed by evaluation of dyebath decolorization (measured by color removal), Chemical Oxygen Demand (COD) variation, among other parameters. Simulated dyebath were prepared and diluted to 5 and 20% of initial concentration. Experimental results confirmed the effectiveness of the procedure in C.I. Reactive Black 5 degradation.

1 INTRODUCTION
Reactive dyes are widely used in the textile industry to color cellulosic fibers [1]. Their reactive groups are able to form covalent bonds with hydroxyl groups on the fiber. A strong covalent bond would be expected but the efficiency of the dye-fiber reaction can change from 90 to 50% [2]. This fact causes a significant problem, considering the residual dye left in the dyebath. Once dyeing is completed, the dyed material is washed off several times in order to remove unfixed and/or hydrolyzed dye. This means that a significant amount of these compounds can be directly lost into wastewaters during processing operations.
Textile industry activities lead to large quantities of textile wastewaters, highly colored and containing a variety of compounds such as dyes, organic chemicals, inorganic salts and others. As most dyes usually occur at low concentrations, when compared with other compounds quantities, it may be presumed that it is not difficult to remove them from textile wastewaters [3]. However, their strong chemical structure is often resistant to several degradation methods, like biological (one of the most used in wastewater treatment) or usual chemical procedures. In the present study, a C.I. Reactive Black 5 commercial dye was considered (molecular structure in Figure 1) in order to establish optimized experimental conditions to dye degradation.

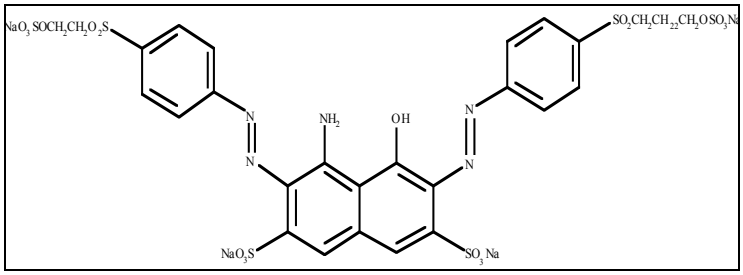

Figure 1: Molecular structure of C.I. Reactive Black 5

Advanced Oxidation Processes (AOP) have been used as an alternative way to textile wastewater treatment, mainly in order to reduce color and organic load. C.I. Reactive Black 5 is a representative diazo dye found in textile wastewaters and several AOPs methods of degradation of this dye have been reported, combined with others like photocatalytic action [4], ultrasound [5], ozone and Fenton's reagent [4].
Hydrogen peroxide is used, for a long time, in decolorization of dyeing wastewater in Advanced Oxidation Processes and also in other procedures, as in electrochemical dye degradation in the presence of cobalt ions [6]. Electrochemical technologies for wastewater treatment are very advantageous considering versatility, environmental compatibility and potential cost effectiveness [7].
In the present work, an Advanced Electrochemical Oxidation Process (AEOP) is discussed concerning the electrochemical degradation of the diazo vinylsulphone reactive dye, C.I. Reactive Black 5, in the presence of hydrogen peroxide and copper ions. The reaction between H_2O_2 and Cu^+ ions (electrochemically generated) leads to hydroxyl radicals production, causing dye oxidation and degradation. H_2O_2 itself requires high concentration and long contact time (even in a electrochemical procedure) but the activation by metals (Fe, Co or Cu) can promote the catalytic decomposition of the oxidant agent, leading to hydroxyl radicals formation. In the present case, the action of copper ions is,

$$Cu^+ + H_2O_2 \rightarrow Cu^{2+} + HO^{\bullet} + HO^-$$

Hydroxyl radicals formation is achieved by chemical means but, to attain this, an initial amount of Cu^{++} ions is added to the solution at the same time as H_2O_2 solution.
A cathodic reaction guarantees Cu^+ production,

$$Cu^{2+} + e^- \rightarrow Cu^+$$

2 MATERIALS AND METHODS

2.1 Dyebath preparation

Simulated dyebaths were prepared according the composition commonly used in cotton dyeing with C.I. Reactive Black 5; it was included in concentration 3% (o.w.f.) and several auxiliary products added to dyebath: Na_2CO_3 (5 gL^{-1}), NaOH 38°Bé (2 mLL^{-1}),

Na_2SO_4 (50 gL^{-1}). The analyzed solutions consisted on 5% and 20% of these initial dyebaths, simulating different textile wastewaters from washing and dyeing procedures.

2.2 Electrochemical procedure

Electrolysis apparatus consisted of a 570 mL closed cell and two Ti/RuO_2 electrodes, 2 cm apart from each other and dipped into the solution. The total effective electrode surface area was 64 cm^2. A power unit Farnell 30-10 controlled the power input. Potential value of 6V was applied in controlled potential experiments. Different volumes of H_2O_2 35% (w/w) were tested, as well various volumes of initial solution of $CuSO_4$ 0.01M for hydrogen peroxide activation. COD, pH, conductivity, redox potential and color measurements were made using standard methods. Experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

For dye degradation study two values of initial dyebath concentration were considered, 5 and 20%. Initial experimental conditions were 4 hours of electrolysis, 4.5 mLL^{-1} H_2O_2 and 7 mLL^{-1} $CuSO_4$. These were the initial conditions in order to study and optimized electrochemical degradation of C.I. Reactive Black 5. Therefore, after electrochemical treatment under those conditions, 5 and 20% solutions presented color removal values indicated in Table 1 and Figure 2.

Table 1: Color removal after 4h of electrolysis

Time (min)	Color removal (%)	
	5% solution	20% solution
30	88.6	89.9
60	90.8	93.1
90	95.3	94.3
120	96.1	95.3
240	97.7	97.8

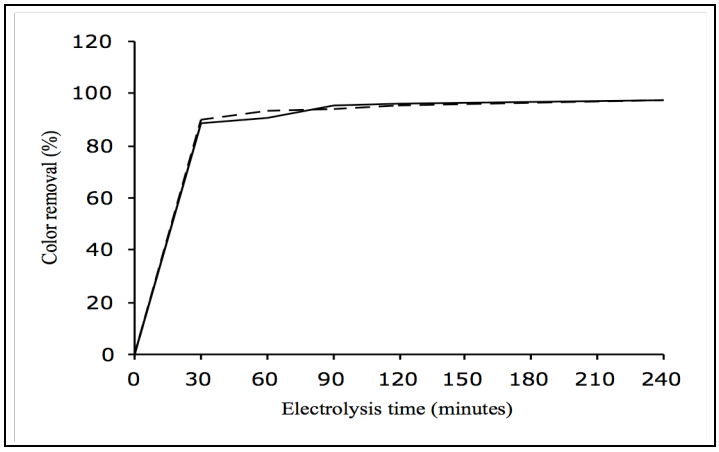

Figure 2: Color removal through 4h of electrolysis (___ 5% sol.; ----- 20% sol.)

In each case (5 and 20% solutions), it was possible to reach an electrolysis time with a considerable color removal value, avoiding long time procedure and too large energy consumption. As a consequence, 90 minutes of electrochemical treatment was considered a suitable time, getting 95.3 and 94.3% of color removal for 5 and 20% solutions, respectively. However, as we can observe in Figure 2, after 60 (or even 30) minutes of electrolysis considerable values of color removal are attained. This fact opens a new perspective for further experiments with very short electrolysis times.
Time factor established, the following step was to reduce $CuSO_4$ and H_2O_2 quantities, in order to optimize electrochemical degradation of C.I. Reactive Black 5 dye. In Tables 2 and 3 results of such a study are presented for 5 and 20% solutions, respectively.
Considering experimental results, it was possible to set the optimized conditions for both solutions in order to attain a color removal over than 90% with a single electrolysis step. For 5% solution, after 90 minutes of electrolysis in the presence of 4.5 mLL^{-1} H_2O_2 and 5 mLL^{-1} $CuSO_4$, 95.5% of decolorization is reached, but also a quite good result (94.8%) is attained with 3 mLL^{-1} H_2O_2 and 3 mLL^{-1} $CuSO_4$. In 20% solution, 4.5 mLL^{-1} H_2O_2 and 7 mLL^{-1} $CuSO_4$ cause 94.2% of color removal, but also a good color removal value (93.4%) is attained with 4.5 mLL^{-1} H_2O_2 and 5 mLL^{-1} $CuSO_4$. On the other hand, increase of H_2O_2 quantity has not a significant improvement in color removal.

Table 2: Color removal for 5% solution after 90 minutes of electrolysis

Sample	H_2O_2 (mLL^{-1})	$CuSO_4$ (mLL^{-1})	Color removal (%)
A_5	4.5	7	94.3
B_5	4.5	5	95.5
C_5	4.5	3	94.8
D_5	4.5	1	92.7
E_5	4	3	94.8
F_5	3	3	94.8
G_5	2	3	94.0
H_5	1	3	93.5

Table 3: Color removal for 20% solution after 90 minutes of electrolysis

Sample	H_2O_2 (mLL^{-1})	$CuSO_4$ (mLL^{-1})	Color removal (%)
A_{20}	4.5	7	94.2
B_{20}	4.5	5	93.4
C_{20}	4.5	3	92.0
D_{20}	4	7	92.0
E_{20}	3	7	92.0
F_{20}	7	7	93.4
G_{20}	15	7	93.0

In Tables 4 and 5 pH, conductivity, redox potential and COD values are presented for 5 and 20% solutions, respectively, after electrolysis in the considered experimental conditions. A significant decrease in COD values is clear in both solutions after electrolysis. Conductivity and pH values do not change considerably. Redox potential is appreciably lower after electrolysis.

Table 4: Analysis of 5% solution after 90 minutes of electrolysis

Sample	H_2O_2 (mLL^{-1})	$CuSO_4$ (mLL^{-1})	pH	Conductivity ($mScm^{-1}$)	Redox potencial (mV)	COD ($mg\ O_2L^{-1}$)
A_5	4.5	7	10.22	5.22	-65	40.1
B_5	4.5	5	8.64	5.25	-61	15.3
C_5	4.5	3	9.32	5.27	-39	31.6
D_5	4.5	1	9.70	5.31	-22	88.4
E_5	4	3	10.23	6.04	-88	47.8
F_5	3	3	9.98	5.93	-90	47.8
G_5	2	3	9.46	5.75	-87	44.5
H_5	1	3	9.87	5.67	-88	51.0

Before electrolysis, average values: pH 9.5; cond. 5 $mScm^{-1}$; Red. pot. 40 mV; COD 81 $mg\ O_2L^{-1}$

Table 5: Analysis of 20% solution after 90 minutes of electrolysis

Sample	H_2O_2 (mLL^{-1})	$CuSO_4$ (mLL^{-1})	pH	Conductivity ($mScm^{-1}$)	Redox potencial (mV)	COD ($mg\ O_2L^{-1}$)
A_{20}	4.5	7	10.76	20.70	-109	158
B_{20}	4.5	5	10.89	20.20	-122	135
C_{20}	4.5	3	10.78	19.81	-153	109
D_{20}	4	7	10.00	20.10	-118	126
E_{20}	3	7	10.33	19.19	-121	142
F_{20}	7	7	10.45	19.31	-132	142
G_{20}	15	7	10.45	20.10	-126	132

Before electrolysis, average values: pH 10.5; cond. 18 $mScm^{-1}$; Red. pot. 6 mV; COD 180 $mg\ O_2L^{-1}$

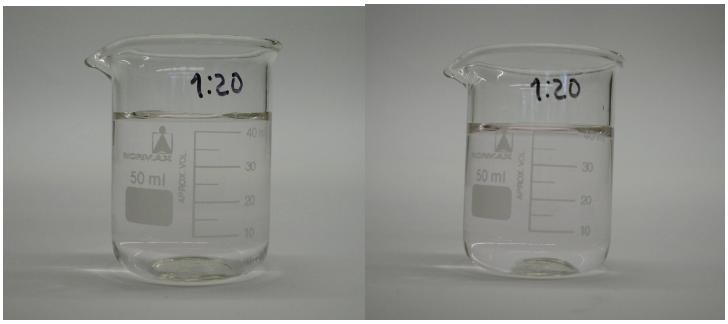

Figure 3: Color removal of samples B_5 and C_5 in a 1:20 dilution

Figure 4: Color removal of samples A_{20} and B_{20} in a 1:40 dilution

4. CONCLUSIONS

Experimental results of this study confirmed that electrochemical procedure is an important alternative for dye degradation in wastewater treatment. In this case, it was possible to demonstrate that oxidation by hydroxyl radicals action, with activation by copper ions produced by cathodic reaction, has an effective result in the case of C.I. Reactive Black 5 dye. The time of 90 minutes for electrochemical procedure was considered a suitable time, getting 95.3 and 94.3% of color removal for 5 and 20% solutions, respectively, when initial experimental conditions were considered, 4.5 mLL^{-1} H_2O_2 and 7 mLL^{-1} $CuSO_4$. A shorter time of electrolysis, 30 or 60 minutes, can also lead to significant decolorization.

Considering experimental results we can also conclude that with established and optimized conditions for electrochemical process it was possible to attained a considerably good level of decolorization of C.I. Reactive Black 5 solutions, with consequently dye degradation. In each case, the final solutions were colorless in a 1:20 or 1:40 dilution (as presented in Figures 3 and 4). In addition, in most situations, total color removal was achieved in both solutions some time after stop electrolysis. This means that a much shorter electrolysis time can also be used only to begin the wastewater treatment procedure and dye degradation. An important detail is also temperature experiments (room temperature), which avoids extra energy consumption.

In almost all situations, COD removal was also considerable, but side reactions could be the cause of some dissimilarity in one of the experimental results. Changes in conductivity and pH values were not significant. Redox potential values showed a very reductive medium after electrolysis.

All results concerned, electrochemical techniques are a very important and efficient option in wastewater treatment and dye degradation in textile effluents, used with or without other procedures.

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